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Rare earth element sources and modification in the Lower Kittanning coal bed, Pennsylvania: implications for the origin of coal mineral matter and rare earth element exposure in underground mines

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Abstract

In this study, we examine the variations in rare earth elements (REE) from the Lower Kittanning coal bed of eastern Ohio and western Pennsylvania, USA, in an attempt to understand the factors that control mineral matter deposition and modification in coal, and to evaluate possible REE mixed exposure hazards facing underground mine workers. The results of this study suggest that the Lower Kittanning coal mineral matter is derived primarily from a clastic source similar to that of the shale overburden. While highly charged cations like silicon, aluminum, and titanium remained relatively immobile within the coal mineral matter, iron (primarily as pyrite) was added from nonclastic sources, either during deposition of the coal mire vegetation or subsequent to burial. Other mobile cations (e.g., alkali and alkaline earth elements) appear to have been added to and/or leached from the originally deposited clastic mineral matter. Most of the sulfur in the Lower Kittanning coal bed is bound as FeS_2 in the mineral matter, but a majority of samples contain a small excess of S that is most likely organically bound.

In general, the total rare earth element content (TREE) in coal ash is greater than that in the shale overburden. If the primary source of mineral matter is the same as that for the overlying shale, then REE must have been enriched in the coal mineral matter subsequent to deposition. The total rare earth element content of Lower Kittanning coals correlates strongly with Si concentration ($[\mathrm{TREE}] \approx 0.0024\ [\mathrm{Si}]$), which provides a threshold for evaluating possible mixed exposure health effects. Chondrite-normalized REE patterns reveal a shale-like light rare earth element (LREE) enrichment for the coal, similar to that of the shale overburden, again suggesting a primarily clastic REE source. However, when normalized to the shale overburden, most of the coal ash samples display a small but distinct heavy rare earth element (HREE) enrichment. We surmise that the HREE were added and/or preferentially retained during epigenesis, possibly associated with groundwater flow through the coal unit, but not necessarily in close association with the addition of iron. At least some of the "excess" HREE could be organically bound within the Lower Kittanning coal.

Keywords: Coal; Geochemistry; Trace elements; Rare earth elements; Lower Kittanning

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1. Introduction

The amount and type of noncombustible mineral matter in coal can have profound effects on the economic viability of a coal bed, and on potential health effects from mining and burning of the coal. The origin of coal mineral matter is poorly understood, although it is thought that depositional (syngenetic) processes (e.g., input of clastic sediments) and postdepositional (epigenetic) processes (e.g., groundwater transport of elements through the peat/coal bed) are important factors (Cecil et al., 1978; Finkelman, 1982; Stach et al., 1982). The use of rare earth elements (REE) in studies of clastic sediment provenance is well established (Nance and Taylor, 1976; McLennan, 1989; Bock et al., 1994), and REE have been used as tracers for seawater, groundwater, and fluid flow processes during diagenesis (Elderfield and Greaves, 1982; Elderfield et al., 1990; Byrne and Kim, 1990; Bau and Möller, 1993; Sholkovitz, 1993; Nath et al., 1997; Johannesson et al., 1999). Therefore, the potential exists for using the REE as tracers to understand both the source and the epigenetic modification of coal mineral matter. Here we examine the variations in REE from a single unit, the Lower Kittanning coal bed of eastern Ohio and western Pennsylvania, USA, in an attempt to understand the factors that control mineral matter deposition and modification in coal. In particular, we seek to address the following questions: (1) What can the REE tell us about the primary source(s) of mineral matter in coal? (2) What is the relationship of coal mineral matter to overlying and underlying sedimentary units? (3) To what extent is the REE content of a coal unit constant, both along strike and at different stratigraphic positions? (4) How do the REE covary with other geochemical parameters in coal, and what does this tell us about the origin and modification of coal mineral matter?

An additional factor motivating this investigation is concern over the possible negative occupational health aspects of rare earth elements, particularly to coal mine workers. While medical data suggest potential health problems related to worker exposures in high-REE environments, there is a lack of understanding regarding how REE exposures affect the human body, and few exposure data indicating concentration levels of REE in mining and related industrial environments (Sulotto et al., 1986; McDonald et al., 1995; Pairon et al., 1995; Hirano and Suzuki, 1996). In underground mines, limitations in airflow can lead to relatively high concentrations of dust. The possibility exists for mixed exposure of REE with other known hazardous particles to worsen mining dust-related illnesses (e.g., coal workers pneumoconiosis, silicosis). In this study, we seek to understand (1) to what extent total rare earth element content can vary within a coal seam; (2) correlations of REE content with other potential sources of health problems; and (3) factors that can be used to predict the occurrence of rare earth element exposure during coal mining operations.

2. Background

2.1. Rare earth elements in coal

The rare earth elements (REE), defined as elements with atomic number 57 (La) through 71 (Lu), are present at the parts per million (ppm) level in most rocks, and have long been used in petrogenetic studies of igneous rocks (see Hanson, 1980, for a review). All of the rare earth elements readily form 3^+ ions under earth surface conditions; in addition, Ce^{4+} can be stable in an oxidizing, low-temperature environment, and Eu^{2+} is stable under certain reducing conditions at high (magmatic) temperatures. This constancy in valence state, when combined with the systematic decrease in ionic radius with increasing atomic number, makes the REE a coherent group of trace elements for tracking petrogenetic sources and processes. The high charge/radius ratio of the REE means that these elements are relatively immobile during weathering, erosion and deposition at the Earth's surface, and thus can be useful for tracking clastic sediment sources.

Rare earth elements in coal appear to consist of a primary fraction which is associated with syngenetic mineral matter (Finkelman, 1982; Palmer et al., 1990). Another portion of the REE can be externally derived or mobilized when primary mineral matter is destroyed or modified, and may be retained in the coal bed but redistributed and incorporated into other mineral components (authigenic minerals). There still exists some disagreement about the proportion of primary and redistributed or authigenic REE in coal (Finkelman, 1982; McLennan, 1989; Mariano, 1989; Ruppert et al., 1993). Although REE are not considered to be highly mobile in low-temperature environments, some researchers have suggested possible mechanisms for mobilizing REE in coal (Eskenazy, 1987, 1999).

The most common mineral groups in coal seams are the aluminosilicates and quartz, sulfur compounds, and carbonates (Stach et al., 1982). It has been suggested that the rare earth elements are associated primarily with fine-grained phosphates (Finkelman, 1982; Willett et al., 2000). However, the REE could also be bound to the surfaces of clay minerals, and may be retained in highly resistant REE-rich trace minerals such as zircon. Although little work has been done on REE in sulfides, pyrite and marcasite could contribute significantly to the overall REE budget (e.g., Yang and Zhou, 2001; Worrall and Pearson, 2001; Zhang et al., 2002). Rare earth element concentrations are generally low in calcium carbonates (Zhong and Mucci, 1995; Sholkovitz and Shen, 1995; Vance and Burton, 1999), but few or no REE data exist on siderite ($FeCO_3$), which is present in the Lower Kittanning coal bed. Selective leaching and particle segregation studies of coals suggest that a portion of the REE may be associated with the organic fraction of coal (Palmer et al., 1990; Willett et al., 2000).

2.2. Potential health problems attributed with REE exposures

Many of the potential occupational health related problems associated with REE exposures appear to be related to pneumoconiosis. Evidence of REE respirable particulates have been found in human lung tissue from patients suffering from this disease (Sulotto et al., 1986; Ruettner et al., 1990; McDonald et al., 1995; Pairon et al., 1995). In each of these cases, the human lung damage was attributed by the researchers to the presence of the respirable REE mineral matter.

The toxicity of REE decreases as atomic number increases, apparently due to greater stability of the heavy rare earth elements (HREE) (Haley, 1991). The toxicity of REE-bearing compounds can also vary widely dependant upon their specific chemical composition (Mogilevskaya and Raikhlin, 1963; Shalgonova, 1967), the most common forms being oxides, chlorides, and fluorides. The substitution of REE for calcium occurs in both geological and biological environments due to the size similarity of their atomic radii. In human bodies, the significant role of Ca in cellular activity may be affected by the presence of REE and the subsequent modification of cellular interactions (Palasz and Czekaj, 2000). Biological response data from the introduction of REE to living laboratory animals have documented lung tissue damage (Mezentseva et al., 1964; Haley, 1991; Shimada et al., 1996). Other possible negative health effects of REE exposures on animal subjects and humans have been reported (Das et al., 1988; Jha and Singh, 1995; Nakamura et al., 1997; Zhu et al., 1997).

Recommended worker exposure limits have been established for the REE based on yttrium (Y) compounds, which behave similarly to the REE. The American Conference of Government Industrial Hygienists (ACGIH) has recommended a threshold limit value (TLV) for Y of 1 mg m^{-3} (time weighted average). There are no data from the mining sector on levels of REE worker exposures, although exposure levels have been reported for plant workers in processing/industrial settings (Singal and Tharr, 1980; Hales and Burr, 1989; Deng et al., 1991).

The National Institute of Occupational Safety and Health has defined mixed exposures as worker exposure to multiple agents in the form of mixtures or as simultaneous but separate exposure modes. Quartz dust in the coal mine environment presents a significant hazard to underground coal mine workers. Research on mining-related silicosis suffered by underground workers has suggested that the amount of quartz matter in a mined seam is not related directly to the mineral composition of the respirable dust fraction produced during mining (Hicks and Nagelschmidt, 1943; Dodgson et al., 1971). Other studies have suggested that the severity of silicosis suffered by mine workers correlates with the rank of the coal (Dodgson et al., 1971) and the composition of the respirable quartz grains which sometimes contained clay coatings (Wallace et al., 1994; Harrison et al., 1997).

Rare earth elements are lithophilic and are often physically associated with clay minerals in coal (Finkelman, 1982; Palmer et al., 1990; Willett et al., 2000). Although the concentrations of REE in most bituminous coals are on the order of tens of ppm on a whole coal basis, the limited space work environment and physical limitations on fresh air movement generally restrict dilution of airborne dusts. Additional contributions to the REE concentrations in coal mine dust can be produced from tonsteins. Tonsteins are quite common in US coal beds and they often have high REE concentrations (in some cases >1000 ppm on an ash basis; Hower et al., 1999; Zhou et al., 2000). It is postulated that REE in dust produced during underground coal mining could constitute a mixed exposure hazard in combination with respirable quartz particles.

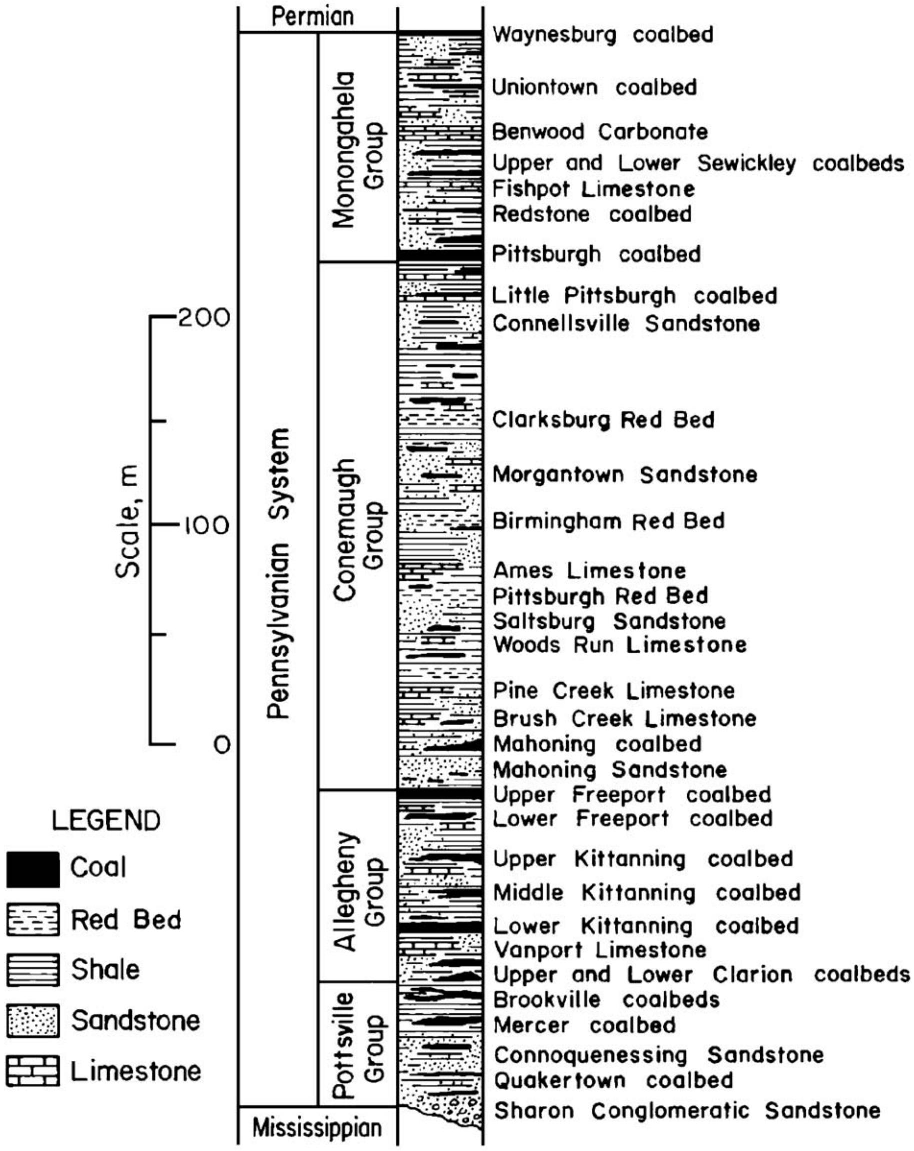


Fig. 1. Generalized Pennsylvanian stratigraphy in the northern Appalachian basin (modified from Puglio and Iannacchione, 1979).

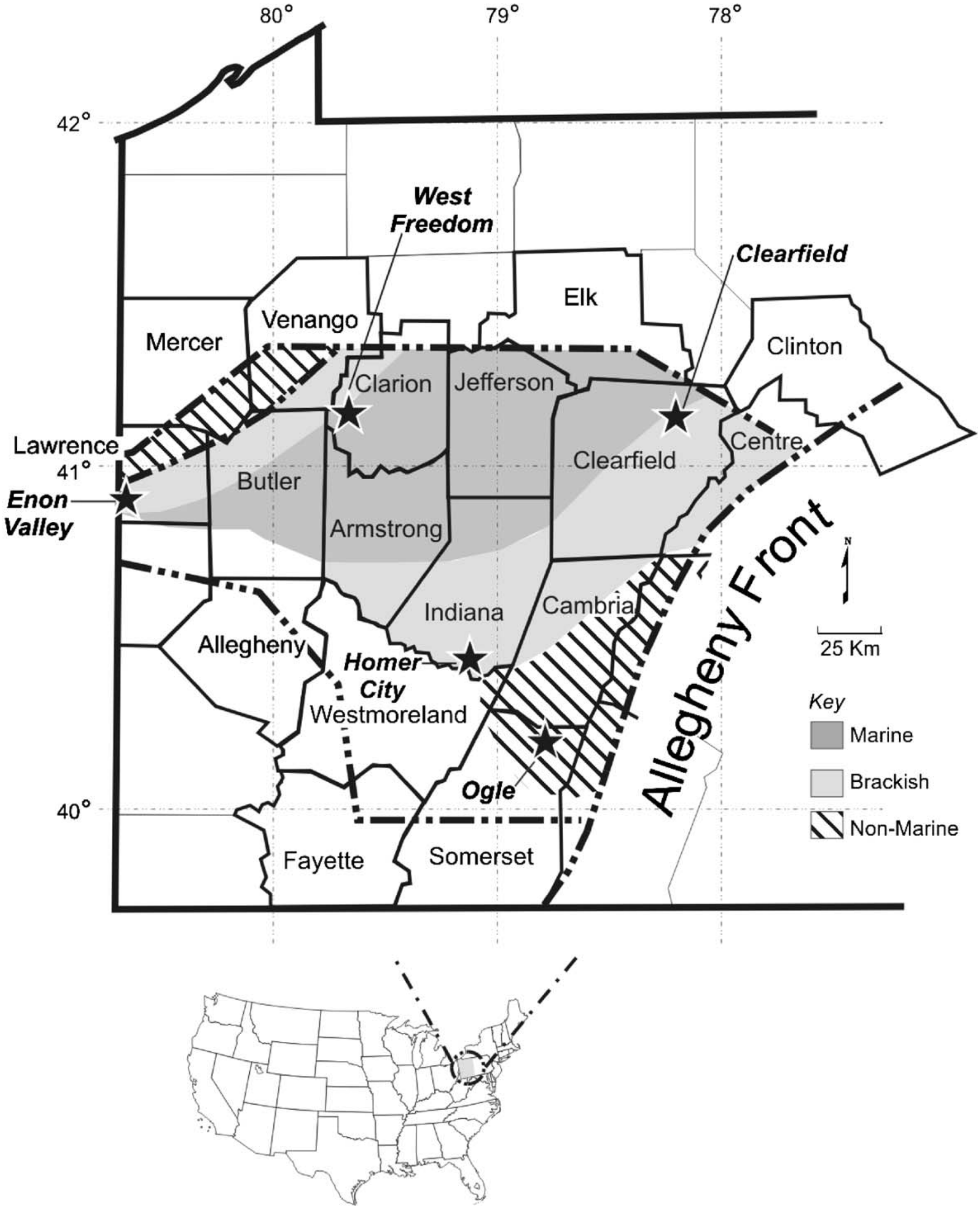


Fig. 2. Map of Lower Kittanning coal bed study sites (indicated by stars) and depositional environment of the shale overburden in western Pennsylvania with county boundaries shown (modified from Rimmer and Davis, 1986).

Table 1
Site locations and sample characteristics

Sample site/location[a]	Sample name	Sample type	Sampling interval (cm)[b]	
			Top	Bottom
Clearfield, Pennsylvania	ocfd00000165	shale overburden	−16.5	0.0
41°03.92′N, 078°24.54′W	ccfd00000070	coal	0.0	7.0
	ccfd00007015	coal	7.0	15.0
	ccfd00015021	coal	15.0	21.0
	ccfd00210290	coal	21.0	29.0
	ccfd00290360	coal	29.0	36.0
	ccfd00360500	coal	36.0	50.0
	ucfd00530640	underclay	53.0	64.0
Enon Valley, Pennsylvania	oevy00000200	shale overburden	−20.0	0.0
40°53.96′N, 080°28.29′W	cevy00000140	coal	0.0	14.0
	cevy00253351	coal	25.3	35.1
	cevy00351451	coal	35.1	45.1
	cevy04510549	coal	45.1	54.9
	cevy00549730	coal	54.9	73.0
	uevy00730870	underclay	73.0	87.0
	uevy02670000	underclay	267.0	n.d.[c]
Homer City, Pennsylvania	ohcy00000185	shale overburden	−29.5	−11.0
40°29.85′N, 079°08.85′W	chcy00000110	shale overburden[d]	−11.0	0.0
	chcy00110162	coal	0.0	5.2
	chcy01620285	coal	5.2	17.5
	chcy02850530	coal	17.5	42.0
	chcy00535970	coal	42.0	48.7
	chcy00591690	coal	48.7	58.0
	chcy00690840	coal	58.0	73.0
	chcy00841115	coal	73.1	100.5
	uhcy11151305	underclay	100.5	119.5
	uhcy21552355	underclay	204.5	224.5
Ogle, Pennsylvania	oogl00000150	shale overburden	−15.0	0.0
40°29.85′N, 079°08.85′W	cogl00000100[e]	coal	0.0	10.0
	cogl00951050[e]	coal	5.0	15.0
	cogl00850950	coal	15.0	25.0
	cogl00574840	coal	25.0	52.6
	cogl00526602	coal	52.6	60.2
	cogl00630900	coal	63.0	90.0
	cogl01020110	coal	102.0	110.0
	uogl00110124	underclay	110.0	124.0
West Freedom, Pennsylvania	owfm00000195	shale overburden	−19.5	0.0
41°05.546′N, 079°37.806′W	cwfm00000073	coal	0.0	7.3
	cwfm00730142	coal	7.3	14.2
	cwfm00142246	coal	14.2	24.6
	cwfm00246320	coal	24.6	32.0
	cwfm00427560	coal	42.7	56.0
	cwfm00560780	coal	56.0	78.0
	uwfm00780820	underclay	78.0	82.0

[a] GPS coordinates based on the Word Geodetic System Survey, 1984.

[b] Given as depth below overburden/coal contact; negative number indicates sample located above contact.

[c] Bottom of sampling interval not recorded.

[d] Originally classified as coal; later found to be organic-rich shale.

[e] Overlapping coal samples taken from two adjacent locations.

2.3. The Lower Kittanning coal

The Lower Kittanning coal bed is within the Allegheny Group (Fig. 1) of the Northern Appalachian basin of Pennsylvania, West Virginia, and Ohio. This coal unit, ranging in thickness from < 0.5 to >1.5 m (Ashley, 1928), was extensively deep-mined from the 1930s through the 1950s in western Pennsylvania. Both surface and subsurface mining of the unit are still taking place. Williams (1960) used fossil assemblages to identify nonmarine, brackish, and marine environments in the shale unit overlying the Lower Kittanning coal bed (Fig. 2). Busch and Rollins (1984) interpreted the stratigraphic variations of the younger Conemaugh Formation to be a result of rapid transgressive events over a planar landscape, with sea level stillstands at coal horizons. This study represented a significant change from prior interpretations based on autogenic modes of coal deposition (Ferm, 1970), and used sequence stratigraphic concepts which were later refined by others to describe Appalachian Basin coal deposition (Cecil et al., 1985; Joeckel, 1995; Eble et al., 2002).

The Lower Kittanning coal bed is interpreted to be Westphalian D in age (Cecil et al., 1985) or about 300 Ma. A transitional period began at the Westphalian C interval which produced a less wet, less tropical

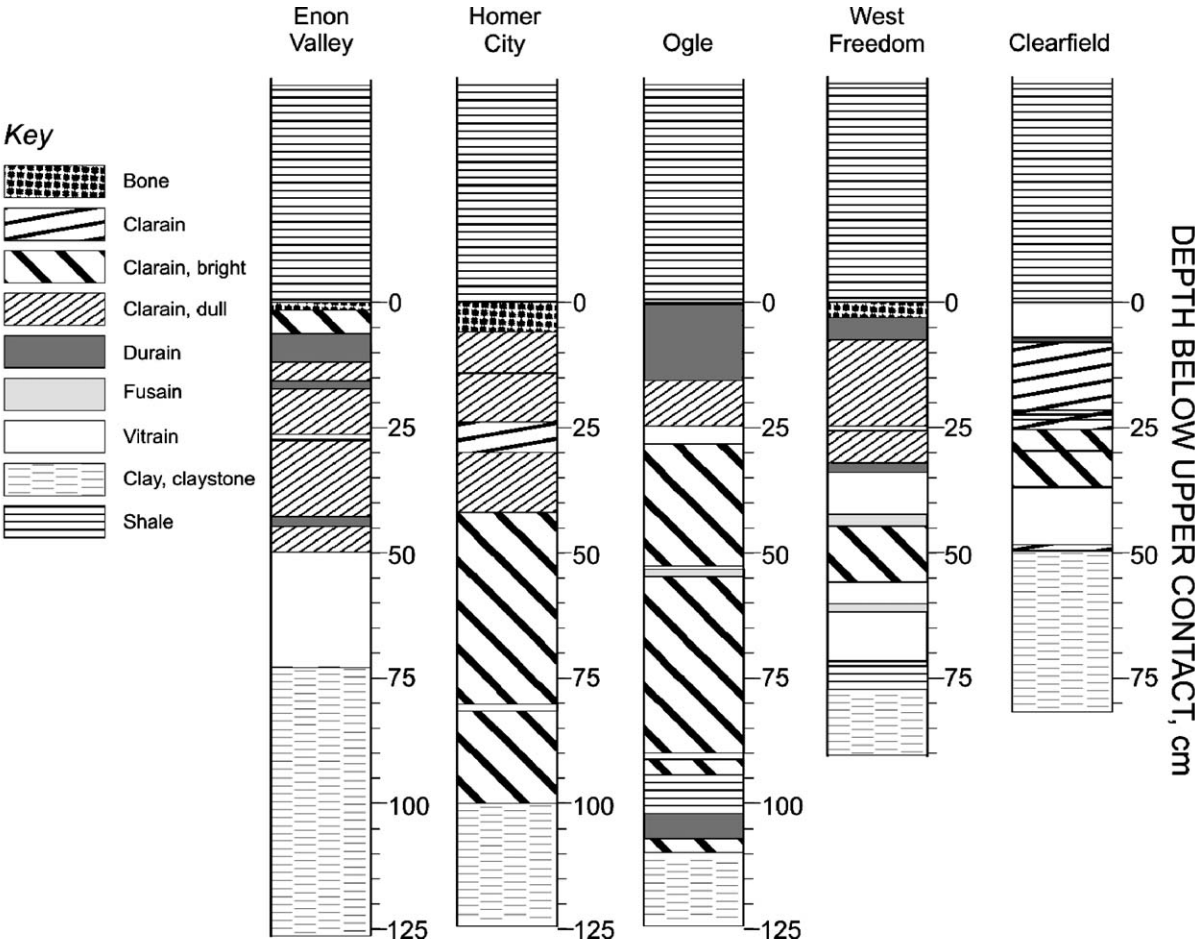


Fig. 3. Coal lithotypes of all studied sites in the Lower Kittanning coal bed. All sites displayed an increase in bright lithotypes towards the bottom of the coal bed.

environment than had persisted through the Early to Middle Pennsylvanian Era (Cecil, 1990). The prevailing depositional environment for the Lower Kittanning coal bed is thought to be primarily a broadly dispersed plain where moisture sources were generally topogenous (Cecil et al., 1985). Deposition occurred during a time of increasing seasonality and aridity as the Appalachian Basin moved away from the equatorial position it occupied prior to about Westphalian C time (Cecil, 1990). The resulting planar mire configurations are classified as having high plant diversity but little species zonation. The Lower Kittanning flora appear to have consisted of lycopods and tree ferns (gymnosperms).

Table 2
Petrographic analysis of coal samples for determination of maceral compostion, rank, and overall mineral content[a]

Field site-sample no.	Basis of analysis	Telinite	Collinite	Vitrinite[b]	Fusinite	Semi-fusinite	Micrinite	Macrinite
Clearfield								
ccfd00000070	OM only	31.6	55.8	87.4	4.2	7.0	1.4	0.0
	Whole coal	26.1	46.1	72.3	3.5	5.8	1.2	0.0
ccfd00015021	OM only	36.1	46.1	82.2	4.1	9.8	2.6	0.0
	Whole coal	33.8	43.2	77.0	3.8	9.2	2.4	0.0
ccfd00360500	OM only	82.2	10.3	92.5	2.6	4.1	0.6	0.0
	Whole coal	74.7	9.4	84.0	2.4	3.7	0.5	0.0
Enon Valley								
cevy00000140	OM only	43.3	40.0	83.3	1.8	1.9	0.9	0.0
	Whole coal	37.9	35.0	73.0	1.6	1.7	0.8	0.0
cevy00351451	OM only	61.7	25.7	87.4	2.5	2.5	1.3	0.1
	Whole coal	56.7	23.6	80.3	2.3	2.3	1.2	0.1
cevy00549730	OM only	67.5	16.8	84.3	6.2	2.6	1.0	0.0
	Whole coal	60.3	15.0	75.3	5.5	2.3	0.9	0.0
Homer City								
chcy00000110[e]	OM only	59.2	16.2	75.4	13.8	9.6	0.0	0.0
	Whole coal	22.1	6.0	28.1	5.1	3.6	0.0	0.0
chcy00285530	OM only	23.9	61.5	85.4	3.3	5.4	3.7	0.0
	Whole coal	21.5	55.2	76.7	3.0	4.8	3.3	0.0
chcy00841115	OM only	78.4	13.1	91.5	5.0	1.8	0.9	t
	Whole coal	71.1	11.9	83.0	4.5	1.6	0.8	0.0
Ogle								
cogl00000100	OM only	38.1	32.3	70.4	6.4	21.4	1.6	0.0
	Whole coal	34.2	29.0	63.2	5.7	19.2	1.4	0.0
cogl00574840	OM only	68.6	24.3	92.9	2.0	4.0	1.0	0.1
	Whole coal	66.4	23.5	89.9	1.9	3.9	1.0	0.1
cogl01020110	OM only	66.5	27.0	93.5	3.2	3.0	0.1	0.0
	Whole coal	39.6	16.1	55.7	1.9	1.8	0.1	0.0
West Freedom								
cwfm00000073	OM only	29.0	40.8	69.8	7.1	10.4	0.9	0.1
	Whole coal	22.8	32.1	55.0	5.6	8.2	0.7	0.1
cwfm00142246	OM only	46.8	40.4	87.2	1.0	0.6	1.0	0.0
	Whole coal	44.1	38.1	82.2	0.9	0.6	0.9	0.0
cwfm00560780	OM only	81.2	11.6	92.8	1.1	0.7	0.0	0.1
	Whole coal	74.2	10.6	84.9	1.0	0.6	0.0	0.1

[a] Volumetric determination.

[b] Sum of vitrinite maceral components.

[c] Parr formula calculation for total mineral matter content.

[d] Measurements in oil, error given of one standard deviation.

[e] Carbonaceous shale.

3. Methods

3.1. Study sites

The study sites are active Pennsylvania mines located in or near the cities of Clearfield, Enon Valley, Homer City, Ogle, and West Freedom (Fig. 2). The sites were chosen to represent coals with overburdens interpreted to be of various depositional environments, from fresh water to marine (Rimmer and Davis, 1986). Rooted (paleosol) underclays were present at the Enon Valley and Homer City sites.

The Clearfield site is an active surface coal mine in which only the Lower Kittanning coal bed is being

Inerto-detrinite	Sporinite	Cutinite	Resinite	Lipto-detrinite	Alginite	MM (%)[c]	R_{max} (%)[d]	R_{random} (%)[d]
0.0	0.0	0.0	0.2	0.0	0.0		1.09 ± 0.05	1.02 ± 0.05
0.0	0.0	0.0	0.2	0.0	0.0	17.3		
0.2	0.1	0.0	0.0	0.0	0.0		1.25 ± 0.03	1.18 ± 0.04
0.2	0.1	0.0	0.0	0.0	0.0	6.3		
0.0	0.1	0.0	0.0	0.1	0.0		1.25 ± 0.04	1.19 ± 0.04
0.0	0.1	0.0	0.0	0.1	0.0	9.2		
0.0	11.2	0.1	0.3	0.0	0.0		0.78 ± 0.04	0.73 ± 0.04
0.0	9.8	0.1	0.3	0.0	0.0	12.4		
0.3	2.8	0.4	1.7	0.0	0.0		0.82 ± 0.04	0.77 ± 0.05
0.3	2.6	0.4	1.6	0.0	0.0	8.1		
0.6	3.2	1.1	0.9	0.1	0.0		0.88 ± 0.03	0.82 ± 0.03
0.5	2.9	1.0	0.8	0.1	0.0	10.7		
1.2	0.0	0.0	0.0	0.0	0.0		1.03 ± 0.03	0.97 ± 0.04
0.4	0.0	0.0	0.0	0.0	0.0	62.7		
0.5	0.2	0.2	0.3	0.0	0.0		1.15 ± 0.03	1.10 ± 0.03
0.4	0.2	0.2	0.3	0.0	0.0	10.2		
0.2	0.3	0.3	t	0.0	0.0		1.15 ± 0.05	1.11 ± 0.05
0.2	0.3	0.3	0.0	0.0	0.0	9.3		
0.2	0.0	0.0	0.0	0.0	0.0		1.58 ± 0.05	1.48 ± 0.07
0.2	0.0	0.0	0.0	0.0	0.0	10.2		
0.0	0.0	0.0	0.0	0.0	0.0		1.66 ± 0.06	1.51 ± 0.08
0.0	0.0	0.0	0.0	0.0	0.0	3.2		
0.2	0.0	0.0	0.0	0.0	0.0		1.49 ± 0.06	1.30 ± 0.06
0.1	0.0	0.0	0.0	0.0	0.0	40.5		
0.9	10.2	0.2	0.4	0.0	0.0		0.86 ± 0.04	0.81 ± 0.04
0.7	8.0	0.2	0.3	0.0	0.0	21.2		
0.0	9.2	0.3	0.6	0.1	0.0		0.81 ± 0.04	0.76 ± 0.03
0.0	8.7	0.3	0.6	0.1	0.0	5.8		
0.2	2.2	0.5	2.4	0.0	0.0		0.91 ± 0.03	0.84 ± 0.05
0.2	2.0	0.5	2.2	0.0	0.0	8.6		

removed. The coal face and overburden were widely accessible for this study but the underclay was not visible. No evidence of prior surface or deep mining was apparent.

The Enon Valley site is an active surface coal and clay mine. The mine operator is removing the Lower Kittanning coal bed, the underlying clay unit, the Vanport Limestone, and the Upper Clarion coal bed (Fig. 1). The coal face was widely accessible for the duration of all site activities and good access was attained to the overburden and underclay units. All of the mined units at the Enon Valley site were intact with no evidence of prior mining.

The Homer City site is a drift underground coal mine. All sampling activity was conducted in a pit which was dug to allow drift access to the Lower Kittanning coal bed. Access to the coal face, the overburden, and the underclay was available. Prior

Table 3
Coal proximate and ultimate analysis summary, dry basis

Sample no.	Ash (%)	Volatile matter (%)	Fixed carbon (%)	C (%)	H (%)	N (%)	S (%)[a]	O (%)[b]	Calorific value (Btu/lb)	Calorific value (MJ/kg)	Calorific value MAF[c] (Btu/lb)	Calorific value MAF[c] (MJ/kg)
Clearfield												
ccfd00000070	20.4	22.2	57.4	65.8	3.9	1.0	5.9	3.0	12,000	27.9	15,000	34.9
ccfd00007015	14.7	23.6	61.8	73.7	4.2	1.1	3.0	3.3	13,200	30.7	15,400	35.8
ccfd00015021	5.7	25.3	69.0	83.1	4.4	1.4	2.1	3.2	14,700	34.2	15,600	36.3
ccfd00210290	9.8	24.9	65.3	76.3	4.4	1.2	6.3	2.1	13,800	32.1	15,300	35.6
ccfd00290360	8.7	24.9	66.5	78.7	4.5	1.2	4.7	2.3	14,000	32.6	15,400	35.8
ccfd00360500	8.3	26.0	65.8	78.7	4.5	1.2	4.2	3.3	14,200	33.0	15,500	36.1
Enon Valley												
cevy00000140	11.4	37.4	51.3	71.5	5.0	1.5	2.8	7.9	12,900	30.0	14,500	33.7
cevy00253351	13.3	34.2	52.6	68.5	4.4	1.4	1.6	10.9	12,300	28.6	14,200	33.0
cevy00351451	7.3	34.8	57.8	75.4	4.8	1.6	2.9	8.0	13,600	31.6	14,700	34.2
cevy04510549	nd[d]	nd[d]	nd[d]	78.4	5.0	1.6	1.5	7.8	nd[d]	nd[d]	nd[d]	nd[d]
cevy00549730	9.8	33.9	56.3	71.4	4.5	1.5	2.1	10.7	13,200	30.7	14,700	34.2
Homer City												
chcy00000110	57.9	14.9	27.2	30.9	2.4	0.4	3.5	4.9	5,500	12.8	13,100	30.5
chcy00110162	23.6	21.5	54.9	65.1	4.0	1.0	1.5	4.8	11,500	26.7	15,100	35.1
chcy01620285	7.9	24.0	68.1	79.4	4.5	1.1	3.7	3.6	14,100	32.8	15,300	35.6
chcy02850530	9.3	24.8	65.9	79.4	4.3	1.3	2.3	3.4	14,100	32.8	15,500	36.1
chcy00535970	9.7	25.9	64.4	75.6	4.5	1.2	7.0	2.0	13,700	31.9	15,200	35.4
chcy00591690	4.1	26.9	69.0	84.0	4.9	1.2	1.7	4.1	14,900	34.7	15,600	36.3
chcy00690840	7.5	26.3	66.2	79.5	4.6	1.2	4.3	2.9	14,300	33.3	15,400	35.8
chcy00841115	8.4	27.1	64.5	79.5	4.6	1.3	2.9	3.3	14,200	33.0	15,500	36.1
Ogle												
cogl00000100	9.5	18.0	72.6	80.5	4.2	1.4	0.5	4.0	13,900	32.3	15,400	35.8
cogl00951050	nd[d]	nd[d]	nd[d]	83.4	4.2	1.4	0.5	4.1	nd[d]	nd[d]	nd[d]	nd[d]
cogl00850950	4.4	18.4	77.3	85.7	4.3	1.3	0.5	3.8	14,800	34.4	15,400	35.8
cogl00574840	3.0	18.7	78.4	87.8	4.1	1.4	0.6	3.1	15,100	35.1	15,600	36.3
cogl00526602	4.8	18.2	77.0	85.5	4.3	1.2	0.5	3.7	14,800	34.4	15,600	36.3
cogl00630900	5.0	24.4	70.7	86.0	4.4	1.2	0.6	2.9	14,900	34.7	15,700	36.5
cogl01020110	37.1	17.4	45.6	47.7	2.9	0.6	8.3	3.5	8,700	20.2	13,800	32.1
West Freedom												
cwfm00000073	19.6	31.6	48.9	67.3	4.2	1.3	2.3	5.4	12,000	27.9	14,900	34.7
cwfm00142246	5.3	41.7	53.0	80.7	5.1	1.5	1.8	5.6	14,300	33.3	15,100	35.1
cwfm00560780	7.9	34.3	57.9	77.8	4.9	1.5	1.4	6.6	13,800	32.1	15,000	34.9

[a] Total sulfur.

[b] Oxygen determination by difference.

[c] Mineral matter-ash free.

[d] nd = not determined.

deep mining of the Lower Kittanning did occur in the area but no evidence of this activity was visible in the rock units.

The Ogle site is located at a large surface coal operation that typically mines five coal beds: the Middle Kittanning, Lower Kittanning, Upper Clarion, Lower Clarion, and Brookville coal beds (Fig. 1). The Lower Kittanning was previously underground mined at the site and is generally present only as the remaining coal pillars. Access to the Lower Kittanning coal bed and overburden was good but the underlying clay was not widely visible. The total channel sample had to be integrated from three independent channels (none containing the complete Lower Kittanning thickness) and some error in total thickness may be present in the two topmost coal sample intervals.

The West Freedom site is a large operating surface coal mine in which only the Lower Kittanning coal bed is being removed. Access to the face was generally good for the coal bed and the overlying shale but the underlying clay was not widely visible. Rapid mine advance rates and variable weather conditions limited the duration of access to the face at the highwall.

3.2. Coal and rock description and sampling procedure

The field description of exposed coal faces was done in accordance with the method of Schopf (1960), and coal lithotypes were described following the techniques of Papp et al. (1998). The Schopf (1960) method was modified in that described lithotypes were not followed laterally on the sampled faces. In this study, describing variation in the coal composition at each site was considered a higher priority.

Sample parameters and locations are given in Table 1. The coordinates of each site were determined with a global positioning system (GPS). A relatively flat and complete section of Lower Kittanning coal was selected and the exposed coal on the face was removed to depth of at least 2.5 cm. Using a handheld rock saw, two vertical slots spaced about 10 to 15 cm apart were cut in the coal, the underlying clay and the shale overburden to form the channel. The section was then measured and the coal lithotypes described. After description was complete, the sample sizes and breaks were configured to ensure a high degree of homogeneity of the coal lithotypes in each sample of the

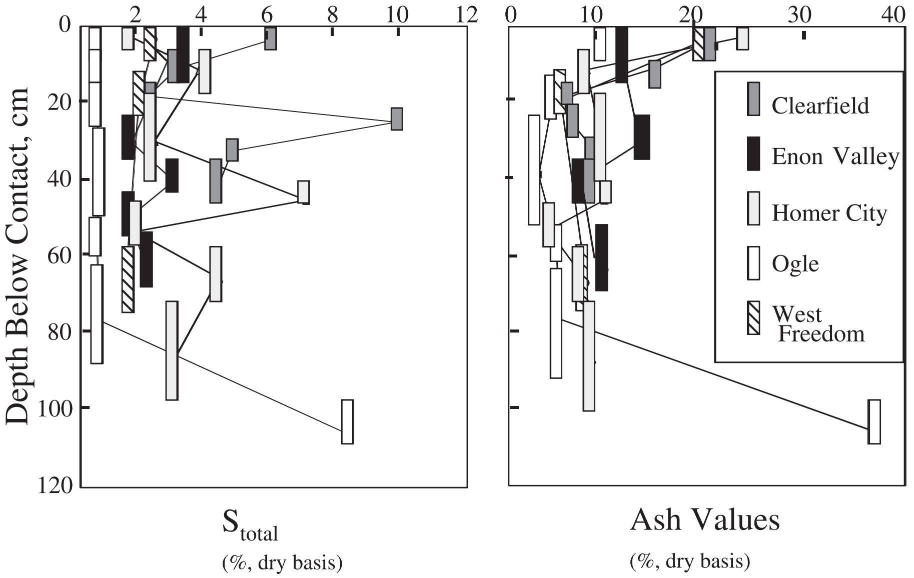


Fig. 4. Total sulfur and ash contents of all Lower Kittanning coal bed sites from proximate and ultimate analysis, plotted against stratigraphic height. The Ogle site was overlain by fresh-water shale and showed consistently low sulfur and ash contents in the main bench of the Lower Kittanning Coal bed. In general, no correlation appears to exist between total sulfur and ash contents in the sample suite.

Table 4
Cation concentrations in overburden shale, underclay, and coal ash[a]

Sample no.	Ash (%)[b]	Si (mg g^{-1})	Al (mg g^{-1})	Fe (mg g^{-1})	Ti (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	Sr (mg g^{-1})	Na (mg g^{-1})	K (mg g^{-1})	P (mg g^{-1})
Clearfield											
ocfd00000165	n/a	240	110	54	3.3	1.6	8.7	0.3	1.5	31	0.7
ccfd00000070	21.0	180	89	210	9.2	5.1	2.5	1.9	0.6	9.3	2.9
ccfd00007015	14.9	250	96	150	3.0	8.2	1.8	0.8	0.7	6.0	0.5
ccfd00015021	5.9	150	130	230	3.2	22.0	2.4	0.9	0.4	1.6	0.6
ccfd00210290	6.6	78	61	250	2.4	8.0	1.2	0.3	0.8	3.6	0.3
ccfd00290360	8.9	86	70	390	1.8	12	1.6	0.5	0.7	3.4	0.4
ccfd00360500	8.6	107	83	340	3.3	11	1.7	0.4	1.1	4.9	0.4
ucfd00530640	n/a	300	120	180	4.4	0.8	6.0	0.1	1.5	26	0.4
Enon Valley											
oevy00000200	n/a	230	110	38	3.7	1.6	9.3	0.2	1.5	28	0.6
cevy00000140	11.8	200	120	180	5.0	3.3	4.3	0.4	1.2	17	0.6
cevy00253351	16.5	280	120	63	14	8.8	2.0	3.5	1.2	9.2	7.9
cevy00351451	7.4	140	120	290	3.7	9.3	1.2	0.3	1.3	2.5	2.1
cevy04510549	6.0	180	130	150	3.2	7.2	2.7	0.4	1.9	6.1	0.9
cevy00549730	10.4	190	120	140	5.4	4.3	2.8	0.2	1.6	10	0.8
uevy00730870	n/a	250	130	11	10	2.0	2.9	0.2	0.7	12	0.3
uevy02670000	n/a	260	140	11	7.0	2.1	2.9	0.1	0.8	11	0.4
Homer City											
ohcy00000185	n/a	140	50	150	3.0	1.4	3.3	0.0	0.8	14	0.5
chcy00000110	57.5	240	120	57	8.0	1.4	6.4	0.1	1.2	23	0.3
chcy00110162	24.2	240	140	40	7.2	3.9	3.7	1.3	0.9	13	1.7
chcy01620285	8.1	130	100	300	2.9	11	1.8	1.4	1.3	2.0	1.5
chcy02850530	7.4	190	120	140	10.1	13	1.7	0.6	1.3	1.6	0.4
chcy00535970	10.1	49	50	510	0.8	9.1	1.0	0.4	0.9	0.4	0.3
chcy00591690	4.4	150	130	170	3.2	21	3.2	0.9	8.7	4.7	0.5
chcy00690840	7.0	90	77	380	2.4	12	1.9	0.5	1.4	3.6	0.4
chcy00841115	8.7	130	44	67	2.3	3.4	1.1	0.2	0.6	4.6	0.2
uhcy11151305	n/a	250	130	19	5.8	0.7	2.8	0.2	1.1	16	0.4
uhcy21552355	n/a	260	78	60	5.1	0.8	3.8	0.1	0.9	19	0.1
Ogle											
oogl00000150	n/a	300	74	9.2	5.4	0.3	3.6	0.0	1.1	20	0.0
cogl00000100	9.5	230	100	130	7.0	6.4	2.8	0.2	0.8	9.7	1.0
cogl00951050	6.5	190	160	85	8.0	9.2	1.8	0.4	0.4	2.7	0.9
cogl00850950	4.6	180	170	57	2.0	13	2.0	0.6	5.8	0.9	0.7
cogl00574840	3.4	160	160	42	3.9	19	3.0	0.9	6.3	3.6	0.8
cogl00526602	4.7	230	200	34	10	14	3.7	0.7	2.3	15	0.8
cogl00630900	6.7	180	140	14	7.2	11	3.2	0.6	1.4	15	0.6
cogl01020110	36.9	190	110	160	9.7	1.4	1.4	0.5	0.7	7.6	0.6
uogl00110124	n/a	240	130	27	9.6	0.7	2.0	0.3	0.8	9.1	0.5
West Freedom											
cwfm00000073	20.8	230	120	89	6.2	2.2	7.1	0.2	1.6	24	0.5
cwfm00730142	11.6	210	120	94	5.5	5.1	6.4	0.3	1.7	22	0.5
cwfm00142246	5.8	168	110	180	5.6	15	4.1	0.7	2.2	10	0.4
cwfm00427560	5.7	200	170	69	4.7	14	2.2	3.0	1.1	7.3	5.2
cwfm00560780	8.0	210	150	89	7.9	7.4	9.3	0.5	25	14	0.9
uwfm00780820	n/a	230	130	11	7.6	6.0	4.3	0.5	1.1	18	2.4

[a] Determined by ICP-AES at the University of Pittsburgh.

[b] Ash values only reported for coal samples and for organic-rich shale from Homer City, sample chcy00000110.

Lower Kittanning coal. Samples were then removed with the aid of hand tools, placed in plastic sample bags, labeled and returned to the National Institute for Occupational Safety and Health, Pittsburgh Research Laboratory (NIOSH/PRL) for sample processing. All samples were completely crushed in a tungsten carbide shatterbox, and divided into aliquots for major cation analysis, rare earth element analysis, and proximate/ultimate analysis using a riffle splitter.

3.3. Proximate and ultimate analysis

Proximate and ultimate analyses were conducted in accordance with ASTM procedures D-3172-89 (ASTM, 1996a) and D-3176-89 (ASTM, 1996b), respectively. The analyses were performed by Commercial Testing and Engineering.

3.4. Coal petrography

Coal petrographic samples were prepared in accordance with the requirements specified in ASTM procedure D-2797-85 (ASTM, 1996c). Maceral descriptions include point counts of 1000 points on two surfaces of the polished coal pellets. Descriptions included the identification of (1) the macerals telinite and collinite of the vitrinite maceral group; (2) the macerals sporinite, cutinite, resinite, alginite, and liptodetrinite of the liptinite maceral group; and (3) the macerals micinite, macrinite, semifusinite, fusinite, and inertodetrinite of the inertinite maceral group. It is recognized that the vitrinite group classification used in this study is not consistent with the current International Committee on Coal Petrology (ICCP, 1995) classification system. It is also recognized that the current ASTM classification standard 2799 (ASTM, 2001) does not contain a vitrinite group distinction for individual macerals. The analyses were performed under NIOSH contract specifications by Dr. James Hower of the University of Kentucky.

3.5. Major and minor element analysis

Analyses of major cations in rock and ashed coal samples were carried out at the University of Pittsburgh using a lithium metaborate-fusion technique that was developed for this study. Prior to fusion, coal samples were ashed in covered quartz glass crucibles at 550 °C in a muffle furnace to convert organic C to CO_2. The sample was cooled and reweighed prior to fusion to determine the ash content. In general, there was excellent agreement between percent ash determined in this step and the value determined from proximate analysis. This indicates that the samples were split quantitatively, and that the results of both types of analysis can be directly compared. The fusion technique is based largely on other reported methods (Ingamells, 1966, 1970; Boar and Ingram, 1970; Karacki and Corcoran, 1973; Bock, 1979; Brenner et al., 1980; Jarvis, 1990; Totland et al., 1992). The sample and the alkaline flux were fused at 1000 °C in a graphite crucible in a muffle furnace and then dissolved in a beaker containing a 4% solution of HNO_3. After the solution was thoroughly stirred, the sample was filtered and rinsed into a polypropylene sample container and diluted to a final concentration of 2% HNO_3. The procedure for the fusion of non-coal samples (overburden and underclay) was identical except for the omission of sample ashing prior to fusion.

Major elements in the lithium metaborate fusion samples were analyzed on a Spectro Modula-EOP inductively coupled plasma-atomic emission spectrometer (ICP-AES). Matrix matching was used on all calibration standards. A new method was developed for this research based on existing techniques used in the geochemistry research group and methods described by other researchers (Jarvis, 1990; Jarvis and Jarvis, 1992; Totland et al., 1992). Three repetitions of each analysis were performed and the statistical mean constitutes the reported data. Samples were analyzed for Si, Fe, Al, K, Ti, Ca, Mg, Na, P, Sr, and Ba. The range of the analyte concentrations was based on the USGS Coal Quality Database (Bragg et al., 1997) and was then modified based on early sample analyses to more accurately reflect the elemental range of samples included in the data set. Estimated uncertainty is ± 10% of the reported values for the major cations. Coal standard reference materials NIST 1632b and USGS CLB-1 were dissolved and measured by the same techniques. The reference materials and internal standards were analyzed approximately every 30 min during the analysis of the Lower Kittanning coal and rock samples to verify instrument calibration.

3.6. Rare earth element concentrations

Rare earth element concentrations and the concentrations of certain trace elements were determined by instrumental neutron activation analysis (INAA). Rock samples were crushed and coal samples were ashed at the University of Pittsburgh, and splits were sent to Activation Laboratory (Actlabs) for analysis. Only La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu were measured, but these are sufficient to determine REE patterns and total REE concentrations. At an interval of about every 11 samples, a CANMET MRG-1 standard was co-irradiated with flux wires at a thermal neutron flux of 7×10^{12} n cm^{-2} s^{-1} in the RIFLS site of the McMaster University Nuclear Reactor. After 7 days, the samples were counted on a high purity co-axial GE Detector with a resolution of better than 1.7 keV for the 1332 keV Co-60 photopeak. Using the flux wire monitors, the data were corrected for decay and compared to a calibration developed from multiple international reference materials. Selected samples were recounted and compared to the original in accordance with the laboratory's QA/QC procedure. Estimated reproducibility is better than ± 10% of the measured values except for terbium (± 20%).

The total rare earth element (TREE) content for each of the ash and overburden/underclay samples was calculated by combining the concentrations of the directly measured REE with concentrations of REE that were not measured; the latter were determined by interpolating from the chondrite-normalized patterns of the measured REE. Total REE concentrations in coal were calculated by dividing TREE in ash by the fraction of ash in the coal sample.

4. Results and discussion

4.1. Lower Kittanning coal bed lithotype analysis

Fig. 3 shows the Lower Kittanning coal lithotypes described for each site. The coal lithotype composition at all sites is dominated by clarain and vitrain.

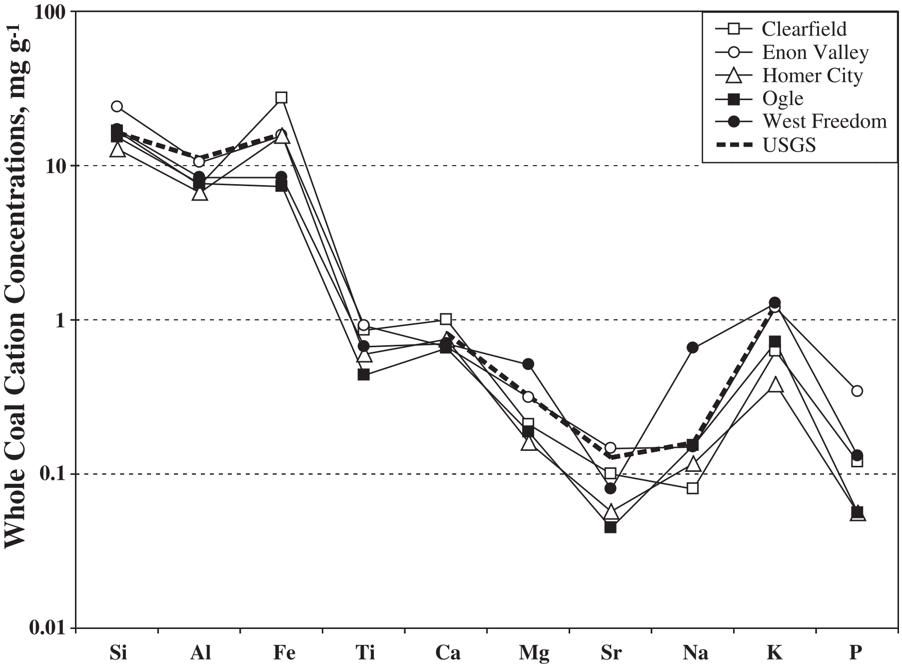


Fig. 5. Cation concentrations on a whole-coal basis, integrated over the entire seam at each sampling site. Also shown for comparison are average data from the lower Kittanning coal seam (dashed line) from the USGS COALQUAL database (85 samples; Bragg et al., 1997). Note that Si, Al and Fe are an order of magnitude higher than any other elements in the coal; this indicates the dominance of aluminosilicates and pyrite in the coal mineral matter.

The clarain compositions are highly variable ranging from about 15% to about 85% bright banding. At all sites, the amount of vitrain and bright clarain increases towards the lower portion of the seam. Most of the sites show a boney, mineral-rich zone frequently enriched in durain towards the top of the seam. The exception is the Clearfield site, where a vitrain band is present at the correlative position in the coal bed. The high mineral matter concentrations may be produced by clastic material associated with the transgressive flooding surface above the coal that terminated coal deposition.

The presence of predominantly bright lithotypes at the bottom of the Lower Kittanning coal and of duller lithotypes at the top of the coal may suggest a "retrograde transition" in a mire migrating from a raised or a slightly raised mire to a planar mire. However, Calder (1993) cautioned against relating bright coal lithotypes to raised mires without other supporting evidence. Substantial organic matter compositional differences exist between modern and ancient peat deposits which complicate analogues made between modern and ancient mires. Some researchers have proposed that the occurrence of duller lithotypes with increased oxidized maceral contents may not necessarily be indicative of increasing dryness or air infiltration, as some maceral oxidation is the result of diagenesis (Teichmüller, 1989). Additional evidence is required to support the concept of a mire in transition (Pierce et al., 1991; Eble and Grady, 1993).

4.2. Petrography

Table 2 shows the results of the coal petrographic analyses. Volumetric concentrations of the vitrinite, inertinite, and liptinite maceral groups are given. Concentrations for the organic matter components are reported both for organic matter only and for the total sample composition. The data indicate a rank range from high volatile B (Enon Valley) to low volatile bituminous (Ogle). This rank in the Lower

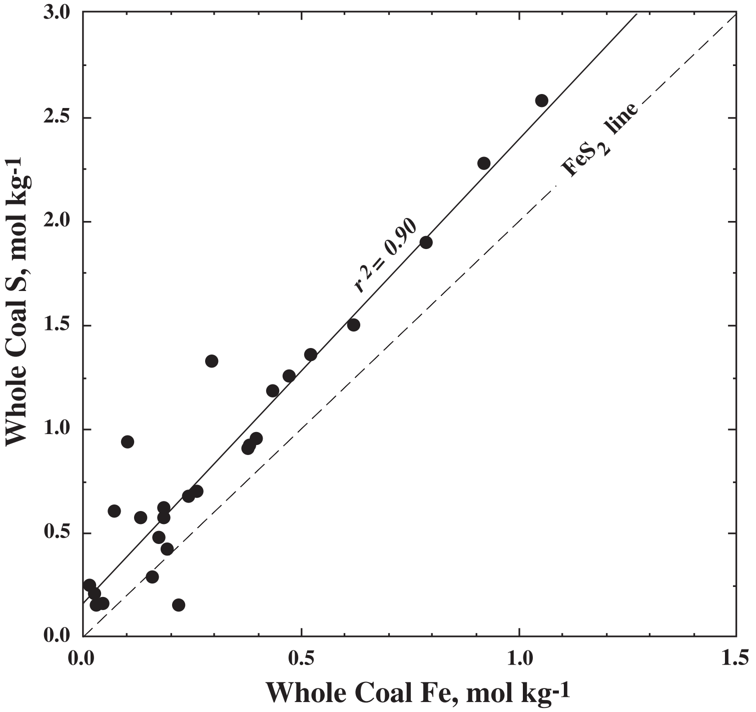


Fig. 6. Comparison of whole-coal concentrations of iron (from ICP-AES) and sulfur (from ultimate analysis) on a molar basis. If all of the Fe and S were in the form of pyrite, the points would fall along the "FeS_2 line." While Fe and S are well correlated, there is an excess sulfur, possibly organically bound.

Kittanning coal bed is consistent with previous observations (Rimmer and Davis, 1988; Rimmer, 1991). Petrographic analyses of samples also suggest that the Lower Kittanning coal bed is compositionally homogenous and that the rank variable is the only one that showed a significant range over the basin. This finding is significant because some of the Lower Kittanning field sites used by Rimmer and Davis (1988) and Rimmer (1991) were also included in this study. Rimmer and Davis (1988) attributed variations in desmocollinite and telocollinite to better preservation of organic matter towards the center of the basin due to more rapid burial and increased subsidence rates, not due to differences in primary organic matter composition.

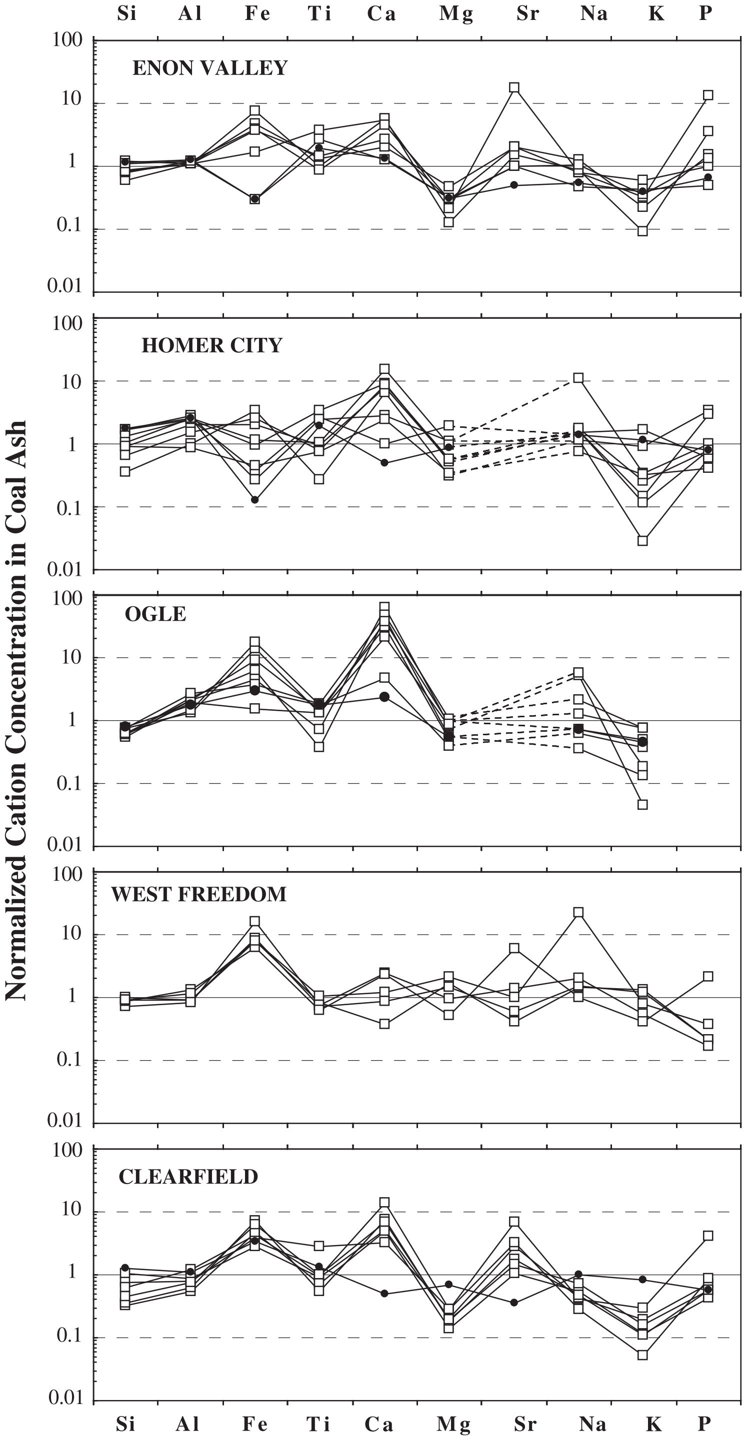
In this coal rank range, the liptinite macerals (sporinite, cutinite, resinite, liptodetrinite, and alginite) are better preserved and much more readily observed during point counts in the low rank samples than in the higher rank samples. Petrographic data from this study confirm a diminished liptinite maceral group content in areas of increased rank in the Lower Kittanning coal bed (Table 2). The gradual alteration of macerals of the liptinite maceral group over vitrinite $R_{\max}$ values of about 0.4% to 1.0% corresponds with the development of the oil window in coal (Brooks and Smith, 1967). All evidence of the liptinite macerals is completely gone in all three petrographic samples from Ogle, PA, which were determined to have $R_{\max}$ values between 1.2% and 1.7%. On this basis, the liptinite maceral group is confirmed to be unsatisfactory for depositional environment interpretation in this study. There is a notable increase in the fusinite and semifusinite macerals (inertinite maceral group) in petrographic samples retrieved from the top of the seam at some of the sites (Table 2). A portion of the fusinite is most likely related to the presence of fires in the coal mire which produce easily transported coal material (Cope and Chaloner, 1985; Collinson and Scott, 1987; Teichmüller, 1989; Scott, 1989; Eble and Grady, 1990; DiMichele and Phillips, 1994; Eble and Hower, 1995; Greb et al., 1999).

4.3. Proximate and ultimate analyses

Data from the proximate and ultimate analyses of Lower Kittanning coal samples are given in Table 3, and sulfur and ash variations are shown in Fig. 4. The wide range of ash and total sulfur values reported for the sample suite is produced in part by the incremental sampling strategy used in this study. Sulfur and ash contents are typically greatest at the top of the coal bed (Fig. 4), but there is otherwise little correlation between total mineral matter (ash) content and total sulfur in the samples. The Ogle site shows relatively constant sulfur contents over the height of the seam except for a sample taken from the lower bench below a siderite-rich shale (see Fig. 3). Ash content of the same samples ranges from 3% to >9% in the main bench, and ash content increases significantly in the sample below the parting. The Clearfield site, located at the easternmost extent of the sampling range, shows much higher sulfur contents and quite consistent high ash contents. The Enon Valley site is the westernmost location and shows ash contents similar to the Clearfield site but with much lower sulfur contents.

These data show that coal at the Ogle site, which is overlain by shale formed in a nonmarine environment (Williams, 1957, 1960), has the lowest total sulfur content (averaging about 0.5% for the main bed). At the West Freedom site where the shale overburden was deposited in a marine environment, total S contents average about 2.2%. The highest sulfur contents in the Lower Kittanning coal bed are associated with the three sites where the overburden was deposited in brackish water (Homer City, Clearfield and Enon Valley), which is consistent with the findings of Rimmer and Davis (1988). The relatively high total S concentrations in the Lower Kittanning coal bed at sites overlain by brackish water shale may be a function of epigenetic pyrite in the coal formed as a consequence of brackish water sulfate availability, reducing conditions, and/or the presence of sulfate-reducing bacteria in the shale depositional environment.

Fig. 7. Cation concentrations in coal ash and underclay normalized to shale overburden at each site (with the exception of West Freedom, in which the ash is normalized to the underclay due to the lack of overburden data). Coal ash is shown with open squares, and the underclay with closed circles. A value of unity indicates that the coal ash (or underclay) has the same concentration as the shale overburden. The relatively immobile elements Si, Al and Ti tend to cluster around unity, indicating derivation from similar sources and an absence of significant addition or leaching removal. The greatest enrichments tend to be in Fe and Ca, and depletions in Mg and K.


Si Al Fe Ti Ca Mg Sr Na K P
Normalized Cation Concentration in Coal Ash
100
10
1
0.1
0.01
ENON VALLEY
HOMER CITY
OGLE
WEST FREEDOM
CLEARFIELD

The total sulfur content of the Lower Kittanning coal bed is presumed to be a combination of syngenetic and epigenetic sulfur, in keeping with the sulfur isotope findings of Spiker et al. (1994) for the Upper Freeport coal bed. In eastern US Pennsylvanian-age coal beds, the majority of pyritic sulfur present can be of epigenetic origin (Spiker et al., 1994). Sulfur values at the Ogle site are generally very low compared to those of the other sites (Fig. 4). This total sulfur behavior could result from the fresh-water conditions and the lower sulfate content (compared to brackish and marine water) during deposition of the overburden. It can also be seen that the lower bench of the Lower Kittanning coal at Ogle exhibits different ash and sulfur characteristics than those of the overlying main seam. This behavior could result from the isolation of the overlying seam from the lower bench. The loss of water from the shale interbed (Fig. 3) may have introduced brackish or marine waters to the underlying lower coal bench, producing a higher sulfur content.

4.4. Major cation analysis of coal and associated rock units

Elemental concentration data for all coal ash, overburden and underclay samples analyzed from each site are given in Table 4. To a first approximation, the mass of coal ash produced in our ashing procedure is equivalent to the amount of mineral matter in the coal. Loss of sulfur and conversion of cations to oxides during the procedure probably leads to a small but systematic difference between the mass of the ash and that of the original mineral matter, with the latter slightly higher than the former. We estimate that this difference is < 10%, which is insignificant compared to the observed variations in major cations and rare earth elements. Composite whole-coal concentrations for all sites (calculated from the % ash values and sample thickness) are shown in Fig. 5. Overall, concentrations of Si, Al, and Fe are at least an order of magnitude higher than other cation concentrations, indicating that most of the mineral matter in the samples is composed of a combination of aluminosilicates and pyrite. A significant portion of the quartz present is thought to be formed authigenically due to the apparent dissolution of primary quartz mineral matter (Cecil et al., 1985; Bennett et al., 1988). While pyrite (noted in macroscopic form at numerous sample sites) makes up a significant fraction of the mineral matter, there are clearly additional sulfur species not bound to Fe. As shown in Fig. 6, concentrations of Fe and S in the coal samples are well correlated ($r^2 = 0.90$), but bulk coal S values generally fall on the high-S side of the FeS_2 line. The quantity of FeS_2 formed in the Lower Kittanning coal appears to have been iron-limited. This suggests the presence of organically bound sulfur as an important component of Lower Kittanning coal units. In some cases, the sulfur "excess" may be partially balanced by iron in the form of siderite, which was also observed at several sample localities. Iron concentrations are highest at the Clearfield site where the overlying shale was classified as a brackish water unit. All three of the brackish water overburden sites show elevated Fe levels in the coal compared to the sites with marine and fresh-water overburden. Magnesium and sodium are highest at the West Freedom site, the only location overlain by marine shales (Fig. 2). These elevated concentrations could reflect an epigenetic mineralization event produced by dewatering of the overburden units.

To understand the source of the mineral matter in the Lower Kittanning coal, we compared coal ash cation concentrations to those in the overburden shale and underclay. In Fig. 7, ash concentrations are normalized to concentrations in the shale overburden, as this is thought to be the best representative of the local clastic source, and to have undergone a minimum of leaching in the acidic coal mire environment. Because no shale overburden data were available for the West Freedom site, we normalized these data to the underclay. A 1:1 correlation between coal ash and shale overburden would suggest, but not require, that (1) the mineral matter is derived from a clastic source similar to that of the overlying shale, and (2) processes occurring subsequent to deposition did not significantly add or remove components. In general, relatively immobile, highly charged cations (Si, Al, Ti) tend to cluster tightly along the 1:1 line. These elements are thought to be derived from fluvial or eolian deposition of silicate material, and would not be expected to be significantly fractionated by syngenetic or epigenetic processes. In contrast, both Fe and Ca are highly variable, and generally enriched in the coal ash relative to the overburden shale. This suggests that Fe and Ca were introduced in part by processes other than clastic deposition. These could include fixation by vegetation in the coal mire, and epigenetic transport into the peat or coal by groundwater. In some cases, elements may have been leached and removed by groundwaters. For example, the most likely source for potassium and magnesium is clastic mineral deposition, but these cations appear to have been leached from the system by post-depositional processes.

4.5. Variations in total rare earth element concentration

Rare earth element concentrations in coal ash, overburden shale, and underclay are given in Table 5, along with calculated total rare earth element (TREE) content. Measurements were made on all sample sites except Homer City. Coal samples analyzed from each site were extracted from the top and bottom of the coal unit and from an intermediate location. Total rare earth element content for coal ash from each channel sample and the overburden is shown as a function of stratigraphic height in Fig. 8. While the shale overburden has relatively constant TREE concentrations, there is clearly significant variation in coal ash concentrations within and between each sampling site. In general, TREE in coal ash is greater than in the shale overburden. If the primary source of mineral matter is the same as that for the overlying shale, then REE must have been enriched in the coal mineral matter subsequent to deposition. Alternatively, non-REE major cations could have been selectively leached from the coal mineral matter, leaving an apparent REE enrichment. However, as discussed earlier, there is little evidence for significant removal of major cations (see Fig. 7). The processes that lead to enrichment of REE in coal mineral matter clearly do not operate uniformly throughout the seam. The large variations in TREE with depth (Fig. 8) suggest the possibility of channelized flow of REE-bearing fluids during or after coalification.

Table 5
Rare earth element concentrations for coal ash and whole rock samples[a]

Sample no.	Sample type	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	TREE[b]
		(ppm)								
Clearfield										
ocfd00000165	overburden	55	104	51	9.2	1.8	1.1	4.2	0.63	260
ccfd00000070	coal ash	120	231	110	20	4.4	3.0	14	2.0	590
ccfd00007015	coal ash	101	201	81	18	3.8	2.8	13	1.9	497
ccfd00360500	coal ash	27	70	54	18	4.5	3.8	15	2.2	276
ucfd00530640	underclay	51	99	42	6.3	1.1	0.9	4.1	0.61	233
Enon Valley										
oevy00000200	overburden	60	113	53	9.2	1.6	0.8	3.7	0.55	272
cevy00000140	coal ash	65	107	55	13	2.9	3.0	14	2.1	332
cevy00351451	coal ash	28	87	65	15	3.4	2.1	5.0	0.75	253
cevy00549730	coal ash	43	100	68	18	4.5	3.5	19	2.8	343
uevy00730870	underclay	74	129	58	10	2.0	1.2	5.2	0.76	319
Ogle										
oogl00000150	overburden	50	94	42	8.2	1.5	1.0	4.5	0.67	233
cogl00000100	coal ash	55	117	54	15	3.6	3.0	17	2.5	341
cogl00574840	coal ash	134	271	142	25	4.9	3.0	8.7	1.3	676
cogl01020110	coal ash	64	144	71	15	3.1	2.3	9.7	1.4	371
uogl00110124	underclay	70	124	55	13	3.0	1.5	5.2	0.79	314
West Freedom										
owfm00000195	overburden	83	150	76	13	2.3	1.2	5.0	0.75	374
cwfm00000073	coal ash	98	200	102	22	4.3	2.6	11	1.6	517
cwfm00142246	coal ash	44	126	85	29	6.4	4.8	15	2.2	415
cwfm00560780	coal ash	94	272	160	40	8.8	6.3	22	3.2	757
uwfm00780820	underclay	114	250	128	30	7.2	5.0	7.9	1.0	649

[a] Concentrations determined by instrumental neutron activation analysis (INAA).

[b] Total rare earth element (TREE) concentrations determined by interpolating from chondrite-normalized patterns.

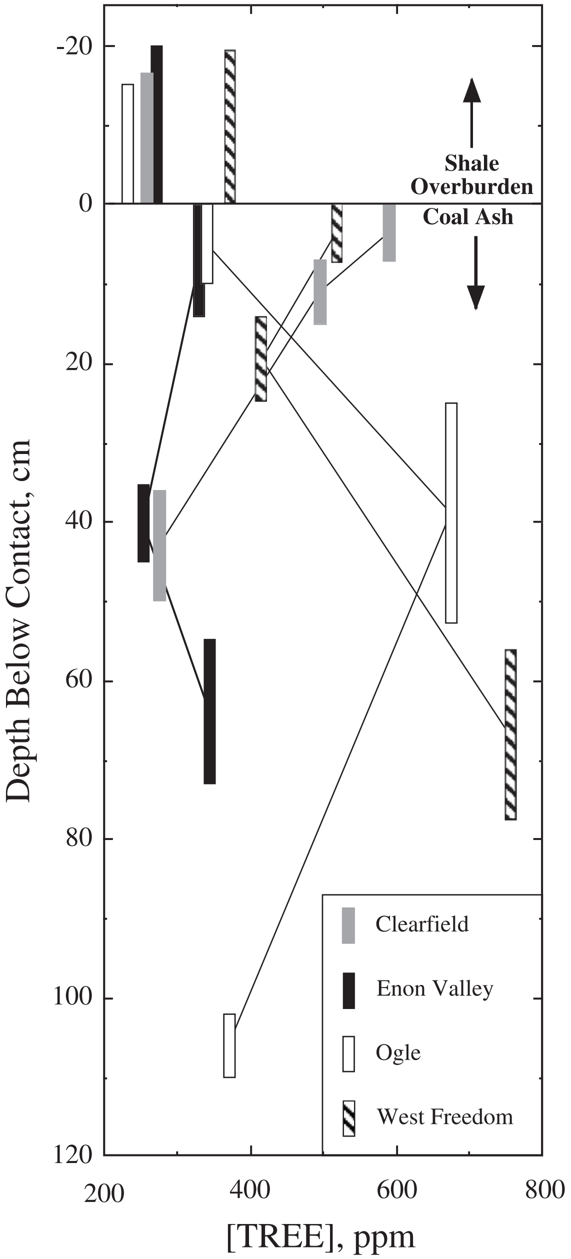


Fig. 8. Total rare earth element (TREE) concentrations in coal ash as a function of stratigraphic height of the channel sample for each Lower Kittanning sample site. Total rare earth element concentrations in coal ash (plotted with depth below coal-shale overburden contact) are highly variable compared to shale at different sites, and generally higher than the shale values.

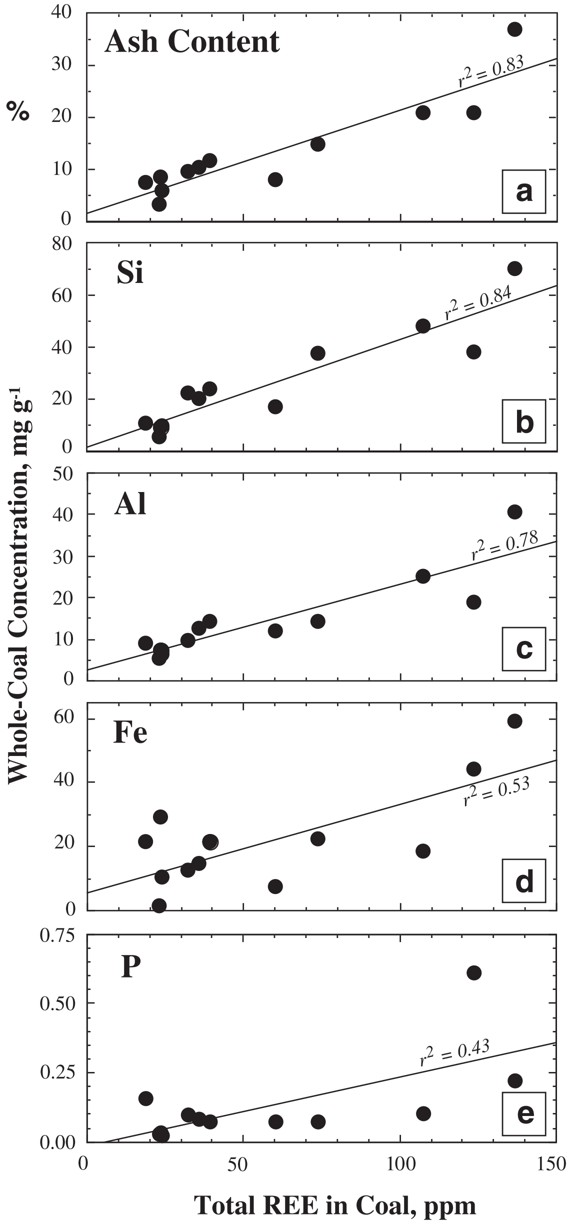


Fig. 9. Total rare earth element (TREE) concentrations on a whole coal basis compared to ash content and selected whole-coal cation concentrations. Correlations with ash content (a) and the major aluminosilicate cations silicon (b) and aluminum (c) are strong, suggesting a link between TREE and clastic input into the coal-forming mire. Correlations with iron (d) and phosphorus (e) are weak, indicating decoupling between these elements and TREE.

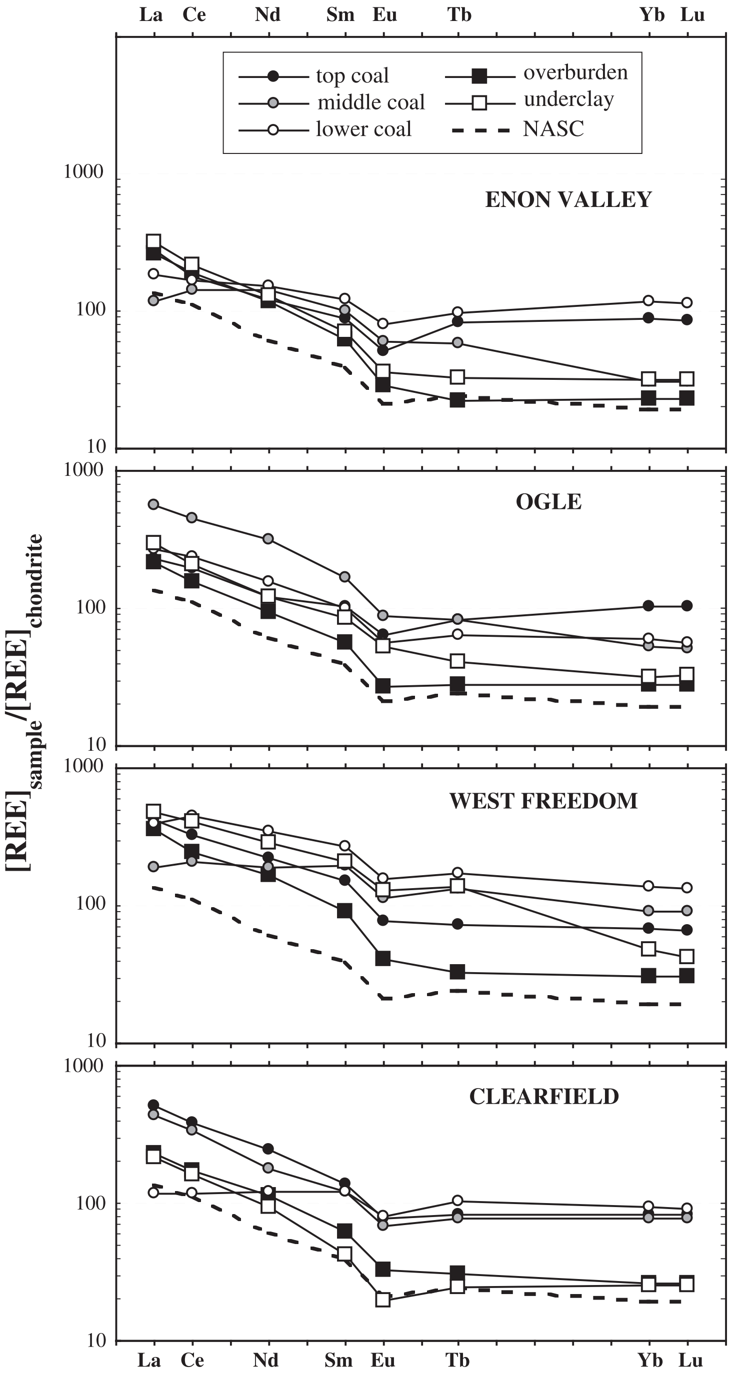


Fig. 10. Chondrite-normalized rare earth element patterns of Lower Kittanning coal ash (circles), shale overburden (closed squares) and underclay (open squares). The North American Shale Composite (NASC; Gromet et al., 1984) is also shown for comparison. In general, the coal ash has shalelike patterns, but at levels somewhat elevated over NASC.

In Fig. 9, the TREE of whole-coal samples (calculated from the ash fraction for each of the coal samples) is compared to ash content and various cation concentrations. There is clearly a correlation of TREE in coal with percent ash (Fig. 9a), indicating that the processes that control REE content are coupled to those that control concentrations of major cations. It is considered reasonable that the total mineral matter content of the coal would not produce a perfect fit to the TREE data because (1) the mineral matter in coal is not identical nor uniformly distributed in the sample suite, and (2) the REE in coal should be preferentially associated certain mineral forms (e.g., clays and phosphates; Finkelman, 1982; Palmer et al., 1990; Willett et al., 2000). Of the major cations, TREE correlate best with Si and Al (Fig. 9b and c). As discussed previously, these elements appear to be derived primarily from input of clastic material into the coal-forming mire; therefore, REE in the Kittanning coals are likely to have a significant clastic component. Moreover, the correlation suggests that the rare earth elements are relatively immobile once they are deposited in the clastic phase.

The covariation of TREE with percent coal ash and with Si is robust, and likely to hold for any coals with significant amounts of mineral matter. Silica is a known culprit in mining-related illnesses (e.g., silicosis), so any mixed exposure enhancement from REE could be significant. For the Kittanning coal, the relationship between Si and total rare earth element content can be approximated as follows:

$$[\mathrm{TREE}] \approx 0.0024[\mathrm{Si}]$$

where both are in the same mass concentration units. Additional work on other coal units is required to determine if this relationship holds in general. Most likely, a linear relationship between TREE and Si will be maintained in other situations, but the enrichment factor could vary significantly. The ratio of [TREE]/[Si] in the overburden shale units tends to be lower than that of the coals, ranging from 0.0008 to 0.0016. This suggests that the REE are enriched in coal mineral matter independently of Si. As discussed earlier, the effects of this level of REE exposure on humans are not currently known.

The correlation of TREE with Fe is significantly weaker than correlations with Si and Al (Fig. 9d). Deviations of iron content from the apparent clastic source (Fig. 7) suggest that Fe is introduced (and possibly removed) by processes other than clastic deposition. For example, dissolved iron in the coal mire environment may be “fixed” with sulfur as pyrite. The processes that introduce Fe do not appear to strongly affect the REE. Thus, REE do not necessarily constitute a good proxy for Fe in coal-forming environments, despite their 3^+ charge. In addition, there is a poor correlation of TREE with phosphorus (Fig. 9e), even though REE are sometimes observed to be hosted in phosphate minerals (e.g., Palmer et al., 1990; Hower et al., 1999). This could result from widely varying REE concentrations in phosphate, or from the presence of other significant REE host minerals. No correlations of TREE with the alkali

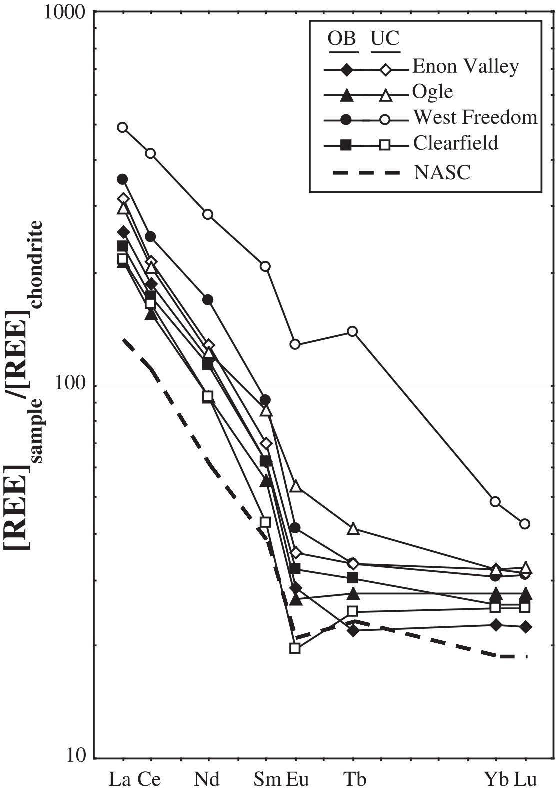


Fig. 11. Chondrite-normalized REE patterns of shale overburden (OB; closed symbols) and underclay (UC; open symbols) compared to the North American Shale Composite (NASC). The overburden samples tend to cluster tightly, while the underclay is more variable. West Freedom, the only site with marine shale overburden, shows the highest REE concentrations in general.

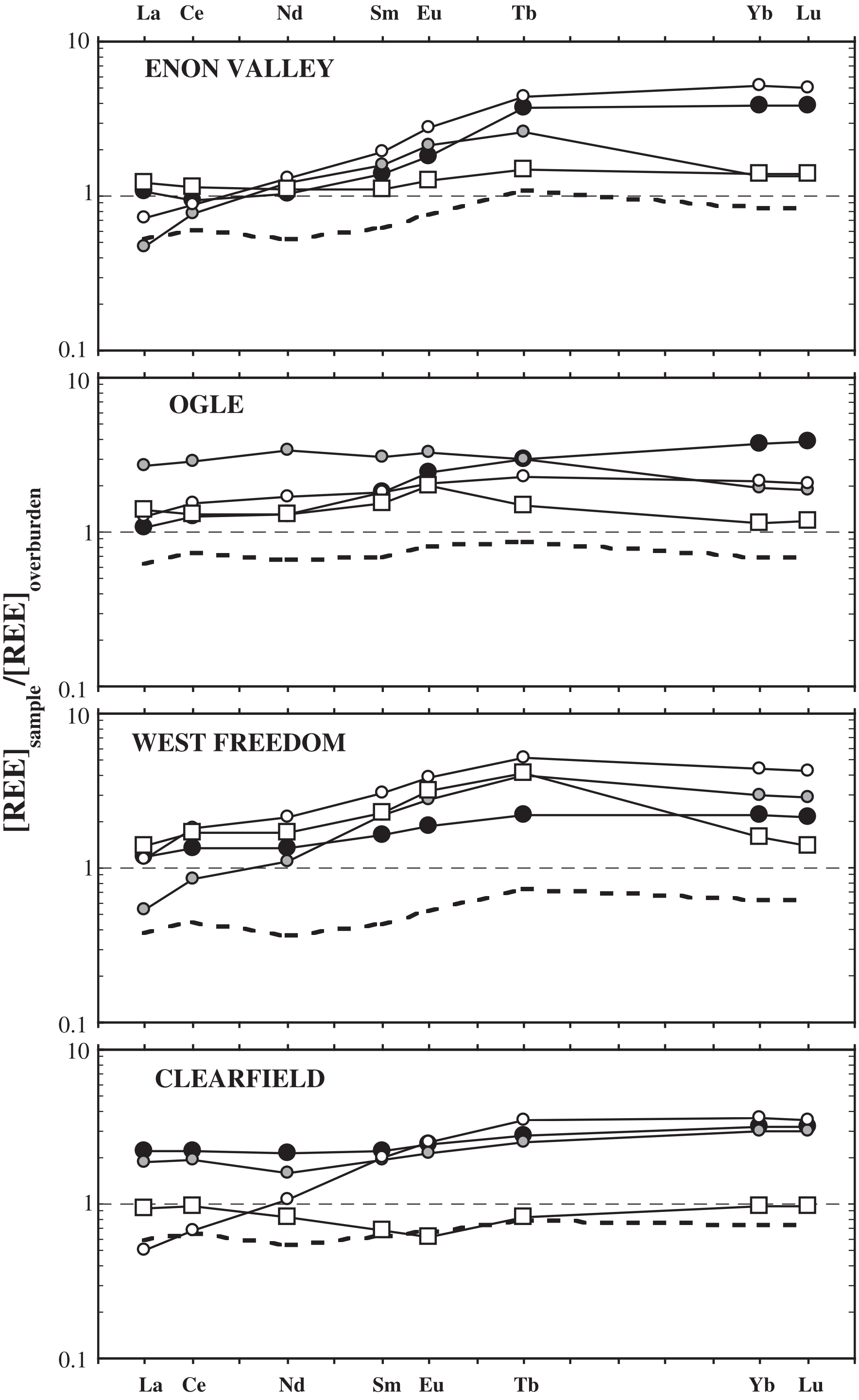


Fig. 12. Coal ash, underclay and NASC rare earth element concentrations normalized to the shale overburden; symbols are the same as in Fig. 10. Most coal ash samples show a significant enrichment in middle- to heavy-REE compared to the overburden.

(K, Na) or alkaline earth (Ca, Mg, Sr) elements were observed; this lack of correlation most likely reflects the very different mobilities of these elements and REE in the syn- and postdepositional coal environments. The primary host mineral for the REE in Kittanning coal units cannot be uniquely determined from these data, but the REE were most likely first introduced as part of the clastic material deposited into the coal-forming mire.

4.6. Sources and modification of rare earth elements

In Fig. 10, individual REE concentrations are shown normalized to chondritic values (Anders and Grevasse, 1989), with the North American Shale Composite (NASC) (Gromet et al., 1984) for comparison. All sites show light rare earth element (LREE) enrichment, a slight negative Eu anomaly, and relatively flat heavy rare earth element (HREE) patterns similar to those of typical shales, but with all concentrations elevated with respect to NASC. These patterns suggest a similar, shale-type source for Kittanning coal mineral matter and surrounding units. Comparison of just the shale overburden and underclay REE patterns (Fig. 11) demonstrates a very tight clustering of the shale overburden REE. These data suggest that the overburden shale source was very similar throughout the Kittanning depositional basin, and that these units are appropriate for normalization of geochemical data (cf. Fig. 7). In addition, preliminary neodymium isotope data (Schatzel and Stewart, 2000) suggest that the overlying shale and coal mineral matter have similar sources. In contrast, the underclay units show considerably more variation in their REE patterns (Fig. 11), possibly reflecting leaching and/or enrichment processes that took place in the acidic environment of the coal-forming mire. In particular, the West Freedom underclay shows significant enrichment in REE. We note that this is the only site overlain by marine shales. However, more data will be required to determine whether or not the depositional environment of overburden causes systematic shifts in REE patterns and abundances of coal mineral matter and surrounding units.

In order to obtain a more detailed comparison of the coal to local sources of clastic material, we normalized coal ash REE concentrations to those of the overburden shale (Fig. 12). In general, coal ash LREE concentrations and patterns are similar to the overburden shale, while the ash has slightly elevated (factor of 2–5) middle rare earth (MREE) and HREE concentrations. Therefore, it appears that the MREE and HREE are enriched in coal samples by a process that does not significantly affect the overlying and underlying shale units. Data from Eskenazy (1999) suggest that HREE may form complexes with organic matter in coal, which then increase the stability of the HREE relative to the LREE. Eskenazy (1999) suggests that HREE are more easily weathered and then preferentially transported in solution because they more readily form soluble bicarbonate and organic complexes compared to LREE. A variety of aqueous sources including sea water and groundwater have shown HREE enrichment (Elderfield and Greaves, 1982; Fee et al., 1992). Some enrichment in REE could also have taken place from root uptake of REE by vegetation in the mire. However, studies of REE uptake by plants have shown no preferential enrichment of HREE or LREE relative to the source (Ran and Liu, 1999; Zhang et al., 2000). The significant HREE enrichment exhibited by the Kittanning coal samples in this study suggests that the HREE were preferentially added to or retained by coal which already contained REE from a clastic source similar to that of the overburden shale. This selective enrichment of HREE took place either by deposition from waters in the original mire, or by epigenetic transport and deposition of REE in groundwaters. The transported REE were incorporated into new or existing minerals, or were organically bound within the coal (e.g., Palmer et al., 1990; Eskenazy, 1999; Willett et al., 2000). As with the shale overburden and underclay, the REE patterns and overall REE concentrations in coal ash do not appear to be systematically related to depositional environment of the overburden.

5. Summary and conclusions

We carried out a petrographic, major element and rare earth element study of the Lower Kittanning coal bed mineral matter collected from sites with a variety of overburden depositional environments. The coal unit is thought to be compositionally homogeneous, although our petrographic study confirms a rank change from high volatile B to low volatile bituminous across the basin. The results of this study suggest that the Lower Kittanning coal mineral matter is derived primarily from a clastic source similar to that of the shale overburden. While highly charged cations like silicon, aluminum, and titanium remained relatively immobile within the coal mineral matter, iron (primarily in pyrite) was added from nonclastic sources, either during deposition of the coal-mire vegetation or epigenetically. Other mobile cations (e.g., alkali and alkaline earth elements) appear to have been added to and/or leached from the originally deposited clastic mineral matter. Most of the sulfur in the Lower Kittanning coal bed is bound as FeS_2 in the mineral matter, but a majority of samples contain a small excess of S that is most likely organically bound. Concentrations of rare earth elements (REE) in coal ash vary significantly (i.e., sometimes more than a factor of two) with stratigraphic height in the coal seam, even from samples at a single site. The total rare earth element (TREE) concentrations of all ash samples from the Lower Kittanning coal bed range from ~ 250 to ~ 750 ppm. A strong correlation of TREE with mineral matter content suggests that a significant portion of the REE are associated with the mineral matter, as suggested by earlier studies (e.g., Palmer et al., 1990). Similar correlations of TREE with Si and Al confirm the link of REE to a clastic mineral component. However, Lower Kittanning coal ash samples almost invariably have higher TREE concentrations than the shale overburden, indicating addition of REE by other processes.

Chondrite-normalized REE patterns show that the coal ash has a shale-like light rare earth element (LREE) enrichment similar to that of the shale overburden and NASC, again suggesting a primarily clastic REE source. However, the coal ash (and underclay) samples display considerably more variability in their REE patterns than the shale overburden, despite the wide range in depositional environments of the latter. When normalized to the shale overburden, most of the coal ash samples display a distinct heavy rare earth element (HREE) enrichment, reflecting addition of HREE to the coal from some source other than clastic deposition. Because TREE correlate poorly with Fe, this addition of HREE does not appear to be tied to the enrichment of Fe in the mineral matter. We surmise that the HREE were added and/or preferentially retained during epigenesis, possibly associated with groundwater flow through the coal unit. Although the speciation of REE cannot be uniquely determined with this study, the complete lack of correlation of TREE with phosphorus argues that epigenetic REE-bearing phosphate minerals may not be the only significant REE host phases. Hence, the ‘‘excess’’ HREE could be organically bound within the Lower Kittanning coal. Overall, REE content and patterns in Lower Kittanning coal ash are not related in any obvious way to the depositional environment of the shale overburden.

The total rare earth element content of Lower Kittanning coals correlates strongly with Si concentration ($[TREE] \approx 0.0024\ [Si]$), which provides a threshold for evaluating possible mixed exposure health effects. Both the REE and Si appear to be relatively immobile in coals, so this correlation is likely to apply to other coal units, with the multiplication factor depending on the [TREE]/[Si] of the clastic source. The distribution of the REE in the Lower Kittanning coal is related to the mineral matter content, and the concentrations of REE determined in the Lower Kittanning coal bed are similar to those reported by other researchers on other bituminous coals. The relationship of TREE content to aluminosilicate and possibly quartz concentrations suggests that REE will often be associated with respirable dust particles of these minerals in underground coal mines. Because the factors controlling silicosis severity in underground coal mines are not clearly understood and the composition of respirable quartz dust particles have been shown to vary and sometimes contain clay, there is the potential for REE to contribute to a mixed exposure health risk.

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